

⑫ **EUROPEAN PATENT SPECIFICATION**

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⑤④ Method and apparatus for preparing a high strength sheet material.

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### Description

The invention relates to a method as defined in the first part of Claim 1 and to an apparatus only for carrying out said method as defined in the first part of Claim 20.

5 Such a method and such an apparatus are described in GB—A—1 526 722.

In spite of the advantages of said known method and apparatus, the laminate manufactured according thereto may have an unsatisfactory rigidity, low temperature tear strength and sealability.

In view of this prior art, it is the object of the invention to provide a laminate having an improved rigidity, an improved tear strength and an improved sealability.

10 Another object of the invention is to provide a laminate which is suitable for use in the production of heavy duty sacks, e.g. sacks for Portland cement.

A further object of the invention is to provide a laminate having an increased yield-point and improved anti-creep properties.

15 In view of these objects, the invention provides the method steps as claimed in Claim 1 and for carrying out these method steps the features of the apparatus of Claim 20.

Some of these method steps are already known through GB—A—1 169 661; according to this publication, a sheet material is heat-treated whereby shrinkage is controlled during heating. This publication, however, refers to the manufacture of non-woven fabrics which are made from fibres, whereby said heat treatment improves the entanglement of said fibres.

20 According to the main aspect of the invention, the biaxially oriented laminate is subjected to a heat treatment while at least 7% shrinkage of the laminate at least in its transverse direction are allowed; the heat treatment is effected by contacting the laminate in a longitudinally pleated state with a hot body; the pleating is adjusted in such an extent that it becomes eliminated by said shrinkage in the transverse direction of the laminate.

25 The invention is based on the discovery that the relatively thin zones of the transversely stretched laminates are overstretched and that the material in these zones exhibit a pronounced tendency to contract when heated to an elevated temperature. Consequently, variations in the thickness of the laminate tend to be reduced or almost eliminated during such a heat treatment.

It is preferred to effect a shrinkage of at least 12% in the transverse direction.

30 The heat treatment may be effected in an oven but in practice it is preferably effected by contacting the laminate with the surface of a heated body because the transverse contraction of the laminate will then occur under more controlled conditions. The heated body is preferably a heated roller.

35 In order to reduce the friction between the laminate under contraction and the heated roller and thus permit that the transverse contraction becomes almost fully even over the width of the laminate, the heat treatment is advantageously effected by contacting a longitudinally pleated laminate with said heated roller. It should be mentioned that a transverse contraction of the laminate may take place after it has left the heated roller but the spontaneous tendency to contract is most pronounced at the start of the heat treatment, i.e., while the laminate is in contact with the heated roller.

40 If the transversely stretched waved laminate is allowed to expand due to its inherent elastic recovery properties before it is subjected to the heat treatment, irregular pleats may be formed and consequently the thermally induced transverse contraction also becomes irregular. Therefore, it is preferred to introduce the laminate onto the heated roller while it still has the waved configuration obtained during the last transverse stretching step. The laminate preferably is allowed to contract longitudinally during said last transverse stretching step. This effect is achieved by keeping a low tension while feeding the laminate into the last transverse stretching device (usually a pair of grooved rollers).

45 This longitudinal contraction improves puncture and tear strength and further improves the form stability of the final product.

50 When the means for transversely stretching the laminate comprise at least one pair of intermeshing grooved rollers, one or more conveyor rollers are preferably arranged between the last pair of intermeshing grooved rollers and the said heated roller, the adjacent rollers in said assembly being in so close proximity to one another that the film is supported by a roller surface during substantially all of its travel from the last pair of grooved rollers to the heated roller.

55 The transverse contraction should preferably be combined with a longitudinal contraction and said longitudinal contraction should be as complete as possible at the annealing temperature used. Therefore, the longitudinal tension in the laminate should preferably be adjusted to a minimum at its introduction onto the hot roller and at the take-off from the hot roller or rollers.

However, when a pleated laminate contacts the hot roller under low tension, air bubbles may be entrapped between said laminate and the roller surface and such air bubbles may lead to an uneven shrinkage.

60 In a preferred embodiment of the method of the invention such entrapped air bubbles are removed by squeezing while allowing the laminate to slide along the surface of the hot roller. This can be achieved in a simple manner by lightly pressing, e.g. by means of a counter roller, the laminate against the surface of the hot roller. More efficiently, however, the entrapped air bubbles are removed by subjecting the laminate to vibrations comprising short intervals during which the laminate is forced against the surface of the hot roller, e.g. by means of a counter roller which is oscillating relative to the hot roller.

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The counter roller is preferably one of the above mentioned transfer rollers.

A second aspect of the invention relates to a particularly advantageous combination of material composition, stretching conditions and a heat treatment.

The method according to this aspect comprises forming a laminate comprising at least two layers of a thermoplastic polymer material, each layer having a fibrillar grain structure providing a predominant direction of splittability in each of said layers, the layers being bonded to one another with the said predominant directions of splittability transverse to each other, and biaxially orienting the molecules of said layers by stretching the layers in substantially uniaxial steps, wherein the thermoplastic polymer material consists of a blend of 40—85% by weight of polypropylene and 60—15% by weight of a lower melting or amorphous admixture which a) mainly consists of polyethylene incl. copolymers thereof, b) exhibits substantially the same or a higher elongation at break than the said polypropylene when tested at room temperature under slow stretching, (c) has a modulus of elasticity which at room temperature is equal to or lower than that of a blend of 90% polyethylene of a density of 0.95 and 10% EPR containing 25% ethylene and 75% propylene, wherein at least the last 25% of the biaxial stretching, measured on the area increase, is carried out below 50°C, and wherein the biaxially oriented laminate is subsequently heat treated at a temperature higher than 50°C, preferably at least 70°C.

By the extrusion of the base films for the laminate, the polypropylene will crystallize (as established by electron microscopy) in the form of fibrils having a diameter of from about 0.5 to 2 microns while the softer polymeric admixture will form a coat on and embedment for these stiffer fibrils. It is well known that polypropylene begins to recrystallize at 50—60°C, whereby the stiffness of the fibrils generally increases. In the combination defined above this stiffening is highly advantageous.

The feature that biaxial stretching (or at least the last part thereof) is carried out at a lower temperature even though the stiffening of the fibrils is desirable, might appear to be an unnecessary complication, but in actual fact this sequence of steps has been found to be very advantageous.

Similar to what is described in connection with the first aspect of the invention, the heat treatment should preferably be carried out under such conditions that at least 7% shrinkage of the laminate takes place in at least its transverse direction, and it should generally be aimed at a higher shrinkage, such as 12% or more.

The use of the special transverse stretching method described as the first aspect of the invention is also advantageous.

Similar to what is well known from high-strength cross-laminates made from uniaxially oriented films, the molecular weight is important as far as the strength is concerned, and generally the melt flow index of the polypropylene should not exceed 1 according to ASTM D 1238 condition L. However, if the molecular weight distribution is particularly even, melt indices up to about 3—4 can be used with good result.

The stretch ratio should preferably not exceed 2.5:1 in any direction, and the optimum ratio is usually between 1.3—1.9, depending on the final use of the laminate. These values refer to the state when shrinkage has taken place (if shrinkage has been effected).

In a preferred embodiment of this second aspect of the invention the admixture comprises as its major component linear polyethylene. While for instance a highly branched polyethylene is less suitable, i.e. due to the fact that its elongation at break at room temperature is substantially lower than that of polypropylene, it has been found that the use of linear polyethylene in such admixture cooperates synergistically with the embedded fibrils of polypropylene (in the stretched and heat treated condition, as defined) to provide particularly advantageous mechanical properties. Furthermore, it has been found that the low stiffening temperature of polyethylene improves the low temperature performance of the laminate to a surprising extent, such that the very pronounced stiffening of polypropylene at temperatures below about 0°C in this case generally becomes an advantage rather than a disadvantage for the mechanical properties of the laminate. In this connection it is important that the admixture which remains soft at the low temperatures is not occluded but on the contrary forms embedment for the stiff polypropylene fibrils.

The linear polyethylene in this embodiment of the invention preferably is high density polyethylene of a melt index according to ASTM D 1238 condition L not exceeding 0.2 and the admixture further comprises a softening component preferably an elastomer.

Alternatively, the linear polyethylene can be low density linear polyethylene. Generally, its melt flow index (ASTM D 1238, condition E), should not exceed 5, and much lower melt flow indices are preferable.

High molecular weight linear low density polyethylene, i.e., of a melt index not exceeding 0.2 (ASTM D 1238 condition L) is particularly advantageous.

The designation "lineary low density polyethylene" or "LLDPE" refers to polyethylene which is branched in controlled manner to achieve a high elongation at break. This controlled branching, as known, can be established, either by a high-pressure polymerization by using a suitable catalyst, or by copolymerization with a suitable branch-forming monomer, such as butene, pentene, hexene or octene, of which the latter is preferable in connection with the present invention.

Advantageously, the polyethylene is selected so that its shrinkability at 100°C, in the oriented state, is higher than the corresponding shrinkability of the polypropylene.

Under these circumstances, a special morphology will result. This morphology is characterized by twists or waves on the polypropylene fibrils with a twist or wave length of the order of 1 micron which can be observed in a scanning electron microscope.

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The mechanical state of this structure has some similarity with cement which is reinforced with prestretched iron.

A third aspect of the invention relates to the manufacture of a laminate having properties which make the material particularly useful for the manufacture of heavy duty sacks.

5 The method according to this aspect comprises forming a laminate comprising at least two layers of a thermoplastic polymer material, each layer having a fibrillar grain providing a predominant direction of splittability in each said layer, the layers being bonded to one another with the said predominant directions of splittability transverse to each other, and biaxially orienting the molecules of said layers by stretching the layers in substantially uniaxial steps, and the method is characterized in that the direction of splittability  
10 of each layer of said layers of the laminate to be biaxially oriented forms an angle of between 10 and 35°C with the machine direction of the laminate.

A sack usually has a width which is much smaller than its length and has been made in such a manner that the machine direction of the thermoplastic film becomes the length direction of the sack.

15 During filling of the sack and regular handling of the filled sack, the most important performance factor is the yield point in its longitudinal direction. In case the filled sack is dropped, the most important performance factors are tear propagation strength, puncture strength and impact strength, the latter under forces which mainly act in the transverse direction of the sack.

It might be assumed that a laminate in which the direction of splittability of each layer is lying relatively close to the machine direction would be weak because a rupture (formed by puncturing or snagging) might  
20 easily propagate under the influence of these transversely acting forces.

The fact, however, is that the opposite is true, namely that the laminate thus produced generally exhibits an advantageous tear propagation resistance in all directions, particularly in the directions which form an angle of 45° to the machine direction. The tear propagation resistance in the said directions has been found determining for the strength of a stitched seam in cross laminated film material, such as a sewn  
25 sack.

An additional advantage obtained relates to the formation of heat seals in the manufacture and/or closing of the sack.

While the laminate can readily be formed into a tube with a glued or heat-sealed longitudinal seam having overlapping edges and a relatively low peel strength is sufficiently in such type of seam, it is  
30 complicated and expensive to fold the material to form overlapping edges at the bottom and/or at the top of the sack. Consequently, there is an important practical need for a high-strength film which readily can be heat-sealed to itself to form seams across its machine direction with a resulting high peel strength.

One measure in this connection is the choice of a suitable surface layer on the laminate.

Another measure is the allowance of a substantial contraction of the laminate perpendicular to the  
35 seam that is parallel to the length of the sack, so that the increased thickness can compensate for the loss of molecular orientation caused by the heat-sealing. At the same time it is essential to limit the contraction of the laminate parallel to the direction of the seam which is perpendicular to the length of the sack.

It has now been found that the melt orientation of the molecules produced in connection with the extrusion (as distinguished from the subsequent biaxial orientation at a much lower temperature) plays a  
40 very important role for the contraction during heat sealing, and that consequently the use of relatively small angles between the machine direction and the directions of splittability (substantially coinciding with the direction of melt orientation) leads to substantially improved heat seals at the top and/or the bottom of the sack, in particular with respect to the impact actions when a filled sack is dropped.

In this third aspect of the invention a heat treatment subsequent to the biaxial stretching is also highly  
45 preferable and similar to what is described in connection with the first aspect of the invention, the heat treatment should preferably be carried out under such conditions that at least 7% shrinkage of the laminate takes place in at least its transverse direction and it should generally be aimed at a higher shrinkage, such as 12% or more.

The use of the special transverse stretching method in connection with the first aspect of the invention  
50 is also advantageous. The stretch ratio should preferably not exceed 2.5:1 in any direction and the optimum ratio is usually between 1.3—1.9 depending on the final use of the laminate. These values refer to the state when shrinkage has taken place (if shrinkage has been effected).

In the practice of this third aspect of the invention, the choice of polymers and heat treatment which are disclosed above in connection with the second aspect of the invention are also advantageously used.

55 Furthermore, this third aspect may advantageously be used in connection with the production of laminates produced in accordance with Claims 22 and 23 of the above mentioned British Patent Specification No. 1,526,722. According to these claims one unoriented two-ply laminate in which the layers exhibit criss-crossing directions of splitability is produced directly by coextrusion, using rotating die-parts. It has now been found that the properties of the final biaxially oriented laminate produced on the basis of this  
60 coextrusion method is substantially improved when the angles between the directions of splittability of each layer and the machine direction fall within the range 10°—35°

Finally, a further aspect of the invention concerns the conservation of the correct amount and kind of bonding between the cross-laminated films, even after a strong heat-treatment.

The method according to the fifth aspect comprises forming a laminate from at least two separately  
65 extruded films of thermoplastic polymer material, each film comprising a) a main layer exhibiting a fibrillar



grain structure providing a predominant direction of splittability in each said film, and b) a second layer for controlling bonding strength, the films being bonded to one another with the said predominant directions of splittability transverse to each other, the second layer of one film facing the second layer of the other film, and biaxially orienting the molecules of said layers by stretching the layers in substantially uniaxial steps, the transverse stretching and the bonding being effected by applying pressure to the surface of the laminate along lines extending substantially in the longitudinal direction of the laminate to impart thereto a waved configuration, and in which main layers the fibrillar grain structure consists of highly crystalline polypropylene and/or high density polyethylene micro fibrils which are generally embedded in a matrix material predominantly consisting of low density polyethylene, and preferably a) said matrix material exhibits an elongation at break similar to or higher than that of the fibrilforming polypropylene or high density polyethylene when tested at room temperature under slow stretch, and b) said second layers mainly consist of branched polyethylene and exhibit a heat-seal temperature higher than 100°C and an elongation at break similar to or higher than that of fibrilforming polypropylene or high density polyethylene.

The branched polyethylene for the second layer preferably is LLDPE, to which there should usually be added about 35% or less of an elastomer, such as ethylene-propylene rubber. The matrix material may also conveniently be based on LLDPE.

When the laminate so produced is heated up to about 100°C—either by a regular heat treatment as described e.g. under the first aspect of this invention, or because hot goods (e.g. hot cement) is packed in the laminate or in sacks made therefrom, the bonding strength will be maintained at the correct, not too high level, which is essential for the achievement of a high tear-propagation resistance.

It is preferred to heat treat the laminate below the temperature at which the second layers heat-seal to each other. The matrix material used preferably has a melting range lower than that of said second layer and the laminate is allowed to shrink, at least in one direction, during said heat treatment.

The extruded films from which the laminate is produced may further comprise a surface layer which facilitates sealing of the laminate. Said layer can with advantage consist of plain or almost plain linearly low density polyethylene.

According to the apparatus of the invention, at least one pair of intermeshing grooved rollers for transverse stretching of a laminate and rollers for longitudinally stretching said laminate are provided.

At least one heated roller is mounted subsequently to said pair of grooved rollers for carrying out the heat treatment as claimed in Claim 1.

It is preferred to place the heated roller in close proximity of the surface of one roller of said pair of grooved rollers to allow the laminate to be contacted with the surface of the heated roller immediately after having left said pair of grooved rollers.

In this manner the fine waved configuration of the laminate is maintained during its travel from the pair of grooved rollers to said heated roller and the contracted laminate resulting from the following heat treatment exhibits very useful strength properties.

One or more conveyor rollers are preferably arranged between the last pair of intermeshing grooved rollers and the said heated roller, the adjacent rollers in said assembly being in so close proximity to one another that the film is supported by a roller surface during substantially all of its travel from the last pair of grooved rollers to the heated roller.

The invention will be further described with reference to Figure 1 of the drawings which schematically illustrates an apparatus for effecting the transverse stretching and heat treatment steps of the method of the invention.

Figure 1 illustrates a roll 1 of a laminate 2, and 3 is a set of grooved rollers. The set of grooved rollers 3 are mounted adjacent to an oscillating roller 4 mounted so close to a hot roller 5 that the laminate 2 is pressed against the surface of the hot roller 5 during short intervals. A cooling roller 6 is also mounted adjacent to the heated roller. The apparatus further comprises a set of take-off rollers 7 and a roll 8 of transversely stretched and heat treated laminate 9.

The operation of the apparatus illustrated is as follows:

Laminate 2 is unwound from the roll 1 and is passed through the nip of the set of grooved rollers 3 in which the laminate is stretched in its transverse direction so as to impart thereto a waved configuration. Following the transverse stretching the laminate is contacted with the oscillating roller 4 and subsequently contacted with the hot roller 5. Due to the oscillating movement of the roller 4 relative to the hot roller 5 the heated laminate is free to shrink longitudinally. After leaving the hot roller 5 the laminate is cooled on cooling roller 6 and is subsequently wound so as to form a roll 8 after having passed through the nip of the set of take-off rollers 7.

The invention will now be described in further detail with reference to the following examples.

#### Example 1

A series of 3-layered tubular films are extruded. Each film has a main layer in the middle, a layer for improved heat sealing on one surface and a layer for improved lamination on the other surface. The three layers form 75%, 15% and 10%, respectively, of the total film.

The main layer consists of a blend (intimately pre-blended in a planetary screw extruder) of

1) a so called "block-copolymer" of propylene and ethylene sold under the trade name "Hostalen 1022",

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2) an ethylene-propylene rubber sold under the trade name "Nordel 1500",

3) a high molecular weight high density polyethylene sold under the trade name "Hostalen 9255 F".

Component 1 has melt flow index of 0.4 according to ASTM D 1238 condition L and analysis shows that it contains about 80% homo-polypropylene, about 10% polyethylene and about 10% ethylene-propylene rubber. A true block-copolymer is hardly detectable by the analysis, but it is very likely that there are undetectable segments of polyethylene on the polypropylene which segments assist in forming a good polymer-in-polymer dispersion.

Component 2 contains about 20% ethylene and exhibits some ethylene crystallinity and a melt index of about 0.3 measured at 190°C but otherwise under the same conditions as in the above mentioned ASTM specification (i.e., at "condition E" instead of "condition L").

Component 3 has a density about 0.95 and melt index of about 0.05 measured under the same conditions as component 2.

The blending ratios appear from the following Table 1:

TABLE 1

| Sample | Code and remarks     | PP-copolymer | True PP. | EPR. admixed | True EPR. | HMW. HDPE admixed | True PE. | Final stretch ratio (after shrinkage, if shrunk), |            | Annealing temperature | Shrink ratio % |       |
|--------|----------------------|--------------|----------|--------------|-----------|-------------------|----------|---|------------|-----------------------|----------------|-------|
|        |                      | %            | %        | %            | %         | %                 | %        | MD  | CD         | °C                    | MD             | CD    |
| a.     | 245,1                | 90           | 72       | 10           | 19        | 0                 | 9        | 1.50:1  | 1.50:1     | (35)                  |                |       |
| b.     | 245,80               | 90           | 72       | 10           | 19        | 0                 | 9        | 1.38:1  | 1.38:1     | 80                    | 20             | 16    |
| c.     | 247,1                | 75           | 60       | 10           | 17        | 15                | 23       | 1.44:1  | 1.56:1     | (35)                  |                |       |
| d.     | 247,80               | 75           | 60       | 10           | 17        | 15                | 23       | 1.44:1  | 1.36:1     | 80                    | 16             | 12    |
| e.     | 255,1                | 65           | 52       | 10           | 16        | 25                | 32       | 1.46:1  | 1.54:1     | (35)                  |                |       |
| f.     | 255,80               | 65           | 52       | 10           | 16        | 25                | 32       | 1.36:1  | 1.36:1     | 80                    | 16             | 16    |
| g.     | 257,1                | 45           | 36       | 10           | 14        | 45                | 50       | 1.54:1  | 1.50:1     | (35)                  |                |       |
| h.     | 257,80               | 45           | 36       | 10           | 14        | 45                | 50       | 1.34:1  | 1.44:1     | 80                    | 18             | 21    |
| i.     | 258,1<br>4 ply.      | 45           | 36       | 10           | 14        | 45                | 50       | 1.60:1  | 1.60:1     | (35)                  |                |       |
| j.     | 258,80<br>4 ply.     | 45           | 36       | 10           | 14        | 45                | 50       | 1.42:1  | 1.44:1     | 80                    | 18             | 16    |
| k.     | 255,13<br>45° grain. | 65           | 52       | 10           | 16        | 25                | 32       | 1.64:1  | 1.64:1     | (35)                  |                |       |
| l.     | 255,803<br>45° grain | 65           | 52       | 10           | 16        | 25                | 32       | 1.46:1  | 1.40:1     | 80                    | 18             | 16    |
| m.     | 255,50               | 65           | 52       | 10           | 16        | 25                | 32       | 1.60:1  | 1.50:1     | 50                    | 8              | 86    |
| n.     | 255,60               | 65           | 52       | 10           | 16        | 25                | 32       | 1.56:1  | 1.46:1     | 60                    | 12             | 11    |
| o.     | 255,70               | 65           | 52       | 10           | 16        | 25                | 32       | 1.40:1  | 1.40:1     | 70                    | 16             | 14.6  |
| p.     | 179,1<br>with LLDPE. | 80           | 64       | 0            | 8         | LLDPE 20          | 28       | 1.56:1  | 1.50:1     | (35)                  |                |       |
| q.     | 179,80<br>with LLDPE | 80           | 64       | 0            | 8         | LLDPE 20          | 28       | 1.40:1  | 1.40:1     | 80                    | 16             | 12.5  |
| r.     | 255,802              | 65           | 52       | 10           | 16        | 25                | 32       | ca. 1.40:1  | ca. 1.40:1 | 80                    | ca. 16         | ca. 3 |

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TABLE 1 (cont.).

| Weight  | Yield point<br>in newton |    | Energy at break<br>newton m. |      | Ultimat<br>tensile strength<br>in newton |    | Elongati n<br>at break<br>% |     |
|---------|--------------------------|----|------------------------------|------|--|----|-----------------------------|-----|
|         | g/sq. m.                 | MD | CD                           | MD   | CD                                       | MD | CD                          | MD  |
| 71      | 27                       | 12 | 14,9                         | 8,9  | 89                                       | 67 | 554                         | 421 |
| 82      | 36                       | 26 | 15,9                         | 10,1 | 85                                       | 55 | 563                         | 538 |
| 76      | 34                       | 14 | 17,8                         | 10,9 | 98                                       | 71 | 596                         | 507 |
| 87      | 36                       | 26 | 18,0                         | 13,5 | 87                                       | 63 | 637                         | 641 |
| 80      | 32                       | 12 | 21,0                         | 7,3  | 104                                      | 54 | 706                         | 410 |
| 98      | 39                       | 28 | 17,9                         | 14,7 | 84                                       | 65 | 636                         | 680 |
| 74      | 27                       | 14 | 15,8                         | 8,5  | 83                                       | 57 | 585                         | 467 |
| 89      | 26                       | 27 | 13,3                         | 7,3  | 52                                       | 50 | 450                         | 391 |
| 96      | 39                       | 19 | 23,1                         | 12,7 | 125                                      | 80 | 658                         | 497 |
| 120     | 42                       | 33 | 26,1                         | 14,1 | 114                                      | 78 | 756                         | 533 |
| 67      | 29                       | 9  | 12,2                         | 6,0  | 80                                       | 49 | 502                         | 392 |
| 88      | 33                       | 25 | 20,5                         | 12,2 | 86                                       | 61 | 780                         | 588 |
| 75      | 31                       | 16 | 14,5                         | 8,0  | 81                                       | 51 | 577                         | 470 |
| 79      | 31                       | 19 | 19,9                         | 9,9  | 98                                       | 54 | 699                         | 543 |
| 92      | 33                       | 23 | 18,2                         | 10,6 | 83                                       | 53 | 703                         | 588 |
| 83      | 40                       | 20 | 19,8                         | 11,8 | 120                                      | 86 | 541                         | 422 |
| 100     | 49                       | 38 | 14,8                         | 12,3 | 95                                       | 77 | 439                         | 448 |
| CA. 100 | 33                       | 32 | 18,0                         | 10,7 | 77                                       | 62 | 744                         | 478 |

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The layer for improved heat sealing consists of 70% "Hostalen 1022" and 30% "Nordel 1500".

The layer for improved lamination consists of 50% "Hostalen 1022" and 50% "Nordel 1500".

The extrusion temperature is 250°C and the blow ratio 1:1.

50 Each of the tubular films is cut helically under an angle of 30° and two such films, each having a width of about 20 cm, are laminated and stretched with the layers for improved lamination facing one another. Initially, the lamination and simultaneous transverse stretching are effected by passing the films six or seven times through the nip between a set of grooved rollers of the type shown in British Patent Specification No. 1,526,722, Figure 7. The division on each roller is 1.8 mm, the width of each tip is 0.4 mm and the tip is circularly rounded. The intermeshing between the tips is 0.9 mm. The stretching is carried out

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at 35°C. Subsequently, each sample is stretched longitudinally at the same temperature by means of rollers.

Stretch ratios are determined by printed marks.

During the longitudinal stretching, the width is reduced significantly.

60 Those samples (as will be described below) which are subjected to heat treatment are over-stretched in the longitudinal direction and finally further stretched in the transverse direction. The aim is that the heat treated samples should end at the same stretch ratios and square meter weight as those which are not heat treated. The pleated configuration created by this last transverse stretching is maintained in the film.

65 Heat treatment is then carried out at various temperatures on 60 cm long and 10 cm wide specimens which are carried forward and backward over a reciprocating heated roller during a period of 120 sec. and under a tension of 300 g. Different temperatures are tried. The specimens are brought in contact with the

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roller while they still have the pleated configuration but the pleats gradually disappear while the material shrinks.

Samples k and l deviate from the above by being cut under an angle of  $45^\circ$  instead of  $30^\circ$ .

Samples i and j deviate in being 4-layered. The angles are as follows:  $+45^\circ$ ,  $+30^\circ$ ,  $-30^\circ$ ,  $-45^\circ$ .

Samples p and q deviate by also being 4-layered materials, with the same directions and further by the composition of the main layer, which is:

80% "Hostalen 1022"

20% linear low density polyethylene of melt index 1.0 and a density of 0.92.

The melt index is measured according to ASTM D 1238 condition L except that the temperature is  $190^\circ\text{C}$ .

Sample r is a 2-ply sample similar to sample f regarding composition, angles and heat-treatment temperature, but deviates by not being subjected to the last transverse stretching and therefore not being in a pleated configuration when it is brought in contact with the hot roller. It is heat treated without any essential transverse contraction, but with longitudinal contraction similar to sample f.

15 mm samples are cut in the machine and cross machine directions of each sample.

Stress-strain diagrams are taken at a velocity of 15 cm per minute and an initial distance of 50 mm between the clamps.

The results obtained will appear from the table and from the diagrams in Figures 2 and 3. The diagrams in Figure 2 compare samples e, f, m and o which all have the same composition and which are treated in the same manner, except that the annealing temperature varies.

The diagrams in Figure 3 compare samples b, d, f and h which contain different percentages of polyethylene, but otherwise are identical, the annealing temperature of this series being  $80^\circ\text{C}$ . In the diagrams of Figures 1 and 2 the values of force and energy are corrected to a gauge of  $80\text{ g/m}^2$ .

As regards the comparison between the sample r which, in essence, was not allowed to shrink transversely, and the similar sample f, which was allowed a significant shrinkage, the table shows that the shrunk film has essentially higher transverse elongation at break and transverse energy absorption, while the two samples have about the same yield point in the transverse direction.

### Example 2

The procedure described in Example 1 is carried out on a number of film compositions, described in Table 2 below, however with the last transverse stretching step and the subsequent heat-treatment taking place in continuous manner on a pilot machine. During this stretching step, the intermeshing of the grooved rollers with each other is adjusted to obtain such a degree of pleating that there will be practically no transverse tension in the film during the heat treatment, but also so that all pleats produced by this stretching disappear due to the transverse shrinkage.

The extrusion temperature is in all cases  $200^\circ\text{C}$  with a blow ratio of 1:1 and a moderate air cooling.

The high-strength laminate are in all cases made from two spirally cut extruded tubular films. Different angles of cutting have been tried, see Table 2.

All steps of stretching are carried out at  $35^\circ\text{C}$ , and the heat treatment is effected on a roller heated to  $80^\circ\text{C}$ . The heat treatment takes about 10 seconds. The laminate is held practically tension-free while being fed in between the last pair of grooved rollers (those which immediately precede the roller for heat treatment). This measure causes the laminate to shrink about 5–10% in the longitudinal direction during the transverse stretching between the grooved rollers. After this stretching, the laminate follows the surface of one of these rollers and is then directly transferred from this surface to the surface of the hot roller, the distance between these surfaces being only about 1 cm. This guided transfer secures that the fine pleats produced by the stretching between the grooved rollers, remain fine and even so as to cause an even transverse contraction on the hot roller.

The latter is driven at a circumferential velocity which is about 10% lower than the circumferential velocity of the last set of grooved rollers. This measure, and a minimum tension at the take-off from the hot roller, gives the laminate a high freedom to shrink longitudinally.

When leaving the hot roller, the laminate is transferred to a cooling roller, after which it is wound up.

The longitudinally and transverse stretch ratios are measured after each step of the process by measuring the deformation of circles, which have been printed on the film before the first stretching step. The aim is a final stretch ratio (i.e., after the heat treatment of 1.40:1 in both directions).

The adjustment of the transverse ratio takes place by the number of transverse stretching steps, which have been varied between 5 and 7 (to which comes the last one before the heat treatment). The adjustment of the longitudinal stretch ratio takes place by variation of the relative velocities of the rollers in the unit for longitudinal stretching. A proper adjustment of the stretch ratios is a complicated matter, and variations between 1.35:1 and 1.45:1 have been tolerated.

The different laminates thus produced are tested for:

- Elmendorf Tear Propagation Resistance according to BS 308 B (43 mm tear),
- Beach Puncture Resistance according to BS 4816:72,
- Falling Dart Impact Strength according to ASTM 1709.



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### Description of the raw materials

The melt flow index (m.f.i.) refers to ASTM D 1238 condition L (in case of polypropylenes) or condition E (in the case of polyethylenes or EPDM).

"Dowlex 2045"

5 LLDPE of density 0,920 and m.f.i.=1.0

"Hostalen 9255"

HMHDPE of density about 0,95 and m.f.i.=about 0.05.

"Hostalen 1050"

homo-PP of m.f.i.=0.4.

10 "Hostalen 1022"

co-PP of m.f.i.=0.4 (further description see Example 1).

"Novolen 1300E"

gas phase-polymerized PP with about 20% contents of atactic PP, partly forming a block-copolymer with the isotactic PP.

15 "Nardel 1500"

EPDM of m.f.i.=about 0.3.

EVA:

An EVA containing about 20% vinylacetate and of m.f.i.=about 5.

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TABLE 2

| Film code No. | Composition  |  |  | Direction of ply degrees | Film weight g/sq m | Falling dart impact strength grams | Elmendorf tear strength (43 mm tear) |                       |                     | Beach puncture resistance, Joules |  |
|---------------|--|--|--|--------------------------|--------------------|------------------------------------|--------------------------------------|-----------------------|---------------------|-----------------------------------|--|
|               | Inner layer (for improved lamination), 10% of total                            | Middle layer 75% of total  | Outer layer (for sealing), 15% of total  |                          |                    |                                    | MD                                   | CD                    | 45°                 | MD                                | CD                                     |
| R402          | 70% "Dowlex 2045"<br>30% "Nordel 1500"   | 80% "Hostalen 1022"<br>20% "Dowlex 2045"   | 100% "Dowlex 2045"                       | 30<br>45                 | 75<br>75           | 500—800<br>600—800                 | 2160+<br>1480                        | 1070<br>1100          | 1340<br>920         | 11.0<br>14.2                      | 9.4<br>13.3                            |
| R404          | "  | 80% "Novolen 1300E"<br>20% "Dowlex 2045"   | "  | 30<br>45                 | 71<br>74           | 600—700<br>600—800                 | 2910+<br>2790+                       | 1450<br>1830          | 1770+<br>1280       | 6.4<br>9.9                        | 9.1<br>13.8                            |
| R407          | "  | 35% "Hostalen 9255"<br>35% "Hostalen 1022"<br>30% "Dowlex 2045"                      | "  | 30<br>45                 | 78<br>85           | 400—700<br>400—600                 | 1620<br>3030+                        | 1870<br>2110          | 2400+<br>2270+      | 11.1<br>7.9                       | 7.0<br>7.5                             |
| R414          | "  | 50% "Hostalen 1022"<br>20% "Hostalen 9255"<br>20% "Dowlex 2045"<br>10% "Nordel 1500" | 70% "Hostalen 1022"<br>30% "Nordel 1500" | 30<br>45<br>60           | 79<br>73<br>71     | 600—900<br>600—800<br>600—800      | 1410<br>1460<br>1660                 | 1430<br>1400<br>2750+ | 2210<br>990<br>1050 | 13.7<br>11.9<br>10.3              | 11.9<br>12.4<br>(average of MD and CD) |
| R417          | "  | 50% "Novolen 1300E"<br>20% "Hostalen 1022"<br>20% "Dowlex 2045"<br>10% "Nordel 1500" | "  | 30<br>45<br>60           | 77<br>82<br>80     | 600—900<br>800—900<br>800—900      | 1280<br>1990<br>1780                 | 1250<br>1460<br>2490+ | 2040+<br>750<br>650 | 11.9<br>13.3<br>12.1              | 12.6<br>14.0<br>13.6                   |
| R419          | "  | 50% "Hostalen 1050"<br>20% "Hostalen 9255"<br>20% "Dowlex 2045"<br>10% "Nordel 1500" | "  | 30<br>45                 | 74<br>71           | 500—700<br>500—800                 | 1670<br>2020                         | 1520<br>1120          | 2050<br>1360        | 10.2<br>11.3                      | 8.5<br>10.5                            |
| R420          | "  | "  | 100% "Dowlex 2045"                       | 45                       | 75                 | 500—800                            | 2450                                 | 1620                  | 1850                | 8.7                               | 7.4                                    |
| R421          | "  | 60% "Hostalen 1022"<br>20% "Hostalen 9255"<br>20% "EVA"                              | "  | 45                       | 77                 | 700—900                            | 500                                  | 2190+                 | 800                 | 12.9                              | 9.9                                    |
| R422          | "  | 50% "Hostalen 1022"<br>20% "Hostalen 9255"<br>20% "Dowlex 2045"<br>10% "Nordel 1500" | "  | 45                       | 84                 | 700—900                            | 2460+                                | 1420                  | 2160+               | 13.6                              | 10.2                                   |
|               | Low density polyethylene (200 µm)<br>Ordinary sack quality film for comparison |  |  |                          | 184                | 500—600                            | 840                                  | 1300                  | 1700                | 5.0<br>(average of MD and CD)     |  |

+ = higher than and indicates that one or more of the single tests exceeded the maximum of the apparatus.

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Several of the samples were further tested for Elmendorf Tear Propagation Strength at  $-15^{\circ}\text{C}$ . For the samples of composition R 407, R 414 and R 419, this gave the same results (within the ranges of accuracy of this method) as the test results at  $20^{\circ}\text{C}$  shown in table 2. This high performance at low temperatures is surprising in view of the high contents of polypropylene, but explicable by the microstructure, which comprises the microscopical to submicroscopical fibrils of stiff polypropylene which are almost entirely embedded in relatively soft polyethylene.

A study of the tear resistance values in relation to the lamination angles (see Table 2) gives the result that the  $45^{\circ}$  laminates show a significant weakness (relatively speaking) in their  $45^{\circ}$  directions, i.e. parallel to the direction of grain in one of the layers.

The same is not true for the  $30^{\circ}$  laminates, which generally show significantly higher all-over tear values, considering that the weakest direction generally determines the value of the laminate with respect to tear propagation resistance.

An exception to the rule that the  $45^{\circ}$  laminates exhibit a relatively low tear propagation resistance along the  $45^{\circ}$  direction, is found in the composition R 407. The main layer (middle layer) of this composition consists of HMHDPE and LLDPE in combination with a PP of significantly lower molecular weight than the HMHDPE, cf. claim 18. It is believed that the improved  $45^{\circ}$  tear strength in this case is due to the advantageous effects explained in the general description in connection with this claim.

Finally, the compositions containing 100% LLDPE in the layers for sealing (i.e., R 402, 404, 407, 420, 421, 422) have been found to form an adequate seal by ultrasonic sealing. The seal resists shear forces up to about 5–6 kp/2.5 mm and peel forces up to about 2 kp/2.5 mm. In this connection it is of importance that the seal layer and the matrix in the middle layer consist of essentially the same material, namely both of a low-density polyethylene type, while the fibrillar, discontinuous, embedded phase of the middle layer consists of the much higher melting polypropylene.

### Example 3

High-strength laminates were produced from two compositions, both entirely consisting of HMHDPE and LLDPE, except for minor amounts of EPDM in the layer for improved lamination. The procedure was identical to that explained in Example 2, except that a prototype machine for full technical scale operation was used.

In both cases, the extrusion temperature was  $240^{\circ}\text{C}$ , the angle of cutting  $45^{\circ}$ , the temperature of stretching  $35^{\circ}\text{C}$ , the temperature of the rollers for heat treatment  $80^{\circ}\text{C}$ , the time of heat treatment about 10 sec. Two heated rollers were used, one after the other, and subsequently two cooling rollers. The final stretch ratio, measured after heat treatment, was about 1.4:1 in both directions.

The entire stretching/lamination process including the heat treatment was operated in-line, the line comprising five transverse stretching stations, one longitudinal stretching station, and the last stretching station supplying the laminate with pleats for the "free-shrinkage" heat treatment. Between the last pair of grooved rollers and the first roller for heat treatment, and in close proximity to both, was an idle roller serving to keep the pleats fine and even.

The transverse stretching ratio was controlled by adjustment of the intermeshing between the grooved rollers in each of the first five pairs of grooved rollers.

As in Example 2, the intermeshing between the last pair of grooved rollers was adjusted to minimize the transverse tension during the heat treatment.

The linearly velocity of the laminate at the exit from the stretching/lamination line was about 30 m/min.

The composition of the films and the results of the laboratory testing appear from Table 3.

The polymer designations and the test methods for impact, tear and puncture resistance are explained in Example 2 above. The other mechanical properties were determined from strain/stress curves taken for 15 mm wide specimens, the initial distance between the draw-clamps being 50 mm.

Strain/stress curves were taken as a modestly low velocity, namely 150 mm/min and at a very low velocity, namely 15 mm/min. The latter was tried in order to study the creep strength.

The yield tension (in Newton/mm<sup>2</sup>) therefore was determined at each of the two velocities, while elongation at break (in %) and ultimate tensile tension (in Newton/mm<sup>2</sup>) were determined only at the velocity 150 mm/min.

The laminate prepared from composition R1 was further converted to open-mouth sacks on commercial sack-making machinery. It was first folded to a flat tube while being side-seamed by use of a commercial hot-melt adhesive, then cut into lengths while being heat-sealed transversely to form the bottom of the sack. This seam was made by simple impulse sealing (without any kind of folding or overlapping) but with the conditions of sealing optimized to allow maximum shrinkage in the longitudinal direction. The dimension of the sack was about 100 cm×50 cm. About 30 of such sacks were filled, closed by overlapping and drop-tested at minus  $20^{\circ}\text{C}$  in competition with sacks of similar size made from a 185 g/sq m low density polyethylene film of standard quality for sack production. By these tests the high-strength laminate was found to be clearly superior in spite of its much lower gauge. The weight of the high-strength laminate used for these bag tests was 80 g/sq m, in other words almost  $2\frac{1}{2}$  times as light as the ordinary polyethylene sack material.

| Film<br>code<br>No. | Composition   |                                    |  | Film<br>weight<br>g/sq m |       |       | Elmendorf<br>tear strength<br>(43 mm tear) |      |      | Beach<br>puncture<br>resistance,<br>Joules |                            |                            | Yield<br>point<br>tension<br>N/mm <sup>2</sup> |      |      | Ultimate<br>tensile<br>tension<br>N/mm <sup>2</sup> |     |     | Elongation<br>at break<br>% |    |     |
|---------------------|---|------------------------------------|--|--------------------------|-------|-------|--|------|------|--|----------------------------|----------------------------|--|------|------|---|-----|-----|-----------------------------|----|-----|
|                     | Inner layer<br>(for im-<br>proved la-<br>mination)<br>10% of to-<br>tal | Middle<br>layer<br>75% of<br>total | Outer lay-<br>er (for<br>improved<br>sealing)<br>15% of to-<br>tal |                          |       |       | MD   | CD   | 45°  | MD   | CD                         | 45°                        | MD   | CD   | 45°  | MD  | CD  | 45° | MD                          | CD | 45° |
|                     |   |                                    |  |                          |       |       |  |      |      |  |                            |                            |  |      |      |   |     |     |                             |    |     |
| R1                  | 70% "Dow-<br>lex 2045"  | 50% "Ho-<br>stalen<br>9255"        | 100% "Dow-<br>lex 2045"  | 74                       | 2020+ | 2360+ | 1360                                       | 10,4 | 13,1 | 12,2                                       | 150<br>mm/<br>min.<br>19,5 | 150<br>mm/<br>min.<br>19,3 | 150<br>mm/<br>min.<br>20,3                     | 51,8 | 43,9 | 30,0  | 603 | 536 | 408                         |    |     |
| R2                  | 30% "Nor-<br>del 1500"  | 50%<br>"Dowlex<br>2045"            |  | 73                       | 3200+ | 3000+ | 2220+                                      | 4,5  | 6,3  | 6,7  | 150<br>mm/<br>min.<br>20,3 | 150<br>mm/<br>min.<br>19,7 | 150<br>mm/<br>min.<br>21,6                     | 49,7 | 48,5 | 26,9  | 536 | 540 | 324                         |    |     |

+ = higher than, and indicates that one or more of the single tests exceeded the maximum of the apparatus.



Claims

1. A method for preparing a high strength sheet material comprising forming a laminate comprising at least two layers of a thermoplastic polymer material, each layer having a fibrillar grain structure providing a predominant direction of splittability in each said layer, the layers being bonded to one another with said predominant directions of splittability transverse to each other, and biaxially orienting the molecules of said layers by stretching the layers in substantially uniaxial steps, the transverse stretching being effected by applying pressure to the surface of the laminate along lines extending substantially in the longitudinal direction of the laminate to impart thereto a waved configuration, characterized in subjecting the biaxially oriented laminate to a heat treatment while allowing at least 7% shrinkage of the laminate to take place in at least its transverse direction, and in effecting the heat treatment by contacting a longitudinally pleated laminate with the surface of a hot body, whereby the laminate is fed onto the said surface in longitudinally pleated state, the pleating being limited to such extent that it becomes eliminated by the said shrinkage in the transverse direction.
2. A method as in Claim 1, characterized in that said heated body is a hot roller.
3. A method as in Claim 1, characterized in introducing onto the heated body a laminate having the configuration obtained during the last transverse stretching step.
4. A method according to Claim 3, characterized in allowing the laminate to contract longitudinally during said last transverse stretching step.
5. A method as in Claim 2, characterized in that air bubbles entrapped between the laminate and the surface of the hot roller are removed by squeezing while allowing the laminate to slide along the surface of the hot roller.
6. A method as in Claim 5, characterized in subjecting the laminate to vibrations comprising short intervals during which the laminate is forced against the surface of the hot roller.
7. A method as in Claim 1, characterized in that the thermoplastic polymer material consists of a blend of 40—85% by weight of polypropylene and 60—15% by weight of a lower melting or amorphous admixture which a) mainly consists of polyethylene incl. copolymers thereof, (b) exhibits substantially the same or a higher elongation at break than the said polypropylene when tested at room temperature under slow stretching, c) has a modulus of elasticity which at room temperature is equal to or lower than that of a blend of 90% polyethylene of a density of 0.95 and 10% EPR containing 25% ethylene and 75% propylene, and wherein at least the last 25% of the biaxial stretching measured on the area increase, is carried out below 50°C, subsequent step of heat treating the biaxially oriented laminate at a temperature higher than 50°C, preferably at least 70°C is provided.
8. A method as in Claim 7, characterized in that the stretch ratio in any direction and determined after shrinkage does not exceed 2.5:1.
9. A method as in Claim 7, characterized in that the admixture comprises as its major component linear polyethylene.
10. A method as in Claim 9, characterized in that the linear polyethylene is high density polyethylene of a melt flow index according to ASTM D 1238 condition E not exceeding 0.2 and that the admixture further comprises between 10 and 50% of a softening component, preferably an elastomer.
11. A method as in Claim 7, characterized in that the linear polyethylene is linear low density polyethylene.
12. A method as in Claim 11, characterized in that the melt flow index of said linear low density polyethylene according to ASTM D 1238 condition E does not exceed 3.
13. A method according to Claim 7, characterized by selecting the polyethylene so that its shrinkability at 100°C, in the oriented state, is higher than the corresponding shrinkability of the polypropylene.
14. A method according to Claim 7, characterized by admixing, as an alloying agent between the polypropylene and the polyethylene, minor amounts of a branched polypropylene, e.g. a copolymer of propylene and a polyolefin with 4 or more carbon atoms.
15. A method as in Claim 1, characterized in that the direction of splittability in each layer of said layers of the laminate to be biaxially oriented forms an angle of between 10 and 35° with the machine direction of the laminate.
16. A method as in Claim 15, characterized in that the stretch ratio in any direction and determined after shrinkage does not exceed 2.5:1.
17. A method as in Claim 1, characterized in that the laminate is formed from at least two separately extruded films of thermoplastic polymer material, each film having a) a main layer exhibiting a fibrillar grain structure providing a predominant direction of splittability in each said film, and b) a second layer for controlling bonding strength, the films being bonded to one another with the said predominant directions of splittability transverse to each other, the second layer of one film facing the second layer of the other film, and biaxially orienting the molecules of said layers by stretching the layers in substantially uniaxial steps, the transverse stretching and the bonding being effected by applying pressure to the surface of the laminate along lines extending substantially in the longitudinal direction of the laminate to impart thereto a waved configuration, and in which main layers the fibrillar grain structure consists of highly crystalline polypropylene and/or high density polyethylene micro fibrils which are generally embedded in a matrix material predominantly consisting of low density polyethylene and further characterized in a) that said

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matrix material exhibits an elongation at break similar to or higher than that of the fibrilforming polypropylene or high density polyethylene when tested at room temperature under slow stretch, b) that said second layers mainly consist of branched polyethylene and exhibit a heat-seal temperature higher than 100°C and an elongation at break similar to or higher than that of the fibril-forming polypropylene or high density polyethylene.

18. A method according to Claim 17, characterized by heat treating the laminate below the temperature at which the second layers heat-seal of each other.

19. A method according to Claim 18, characterized in that said matrix material has a melting range lower than that of said second layer and the laminate is allowed to shrink, at least in one direction, during said heat treatment.

20. An apparatus only for carrying out the method as claimed in Claim 1, comprising at least one pair of intermeshing grooved rollers (3) for transverse stretching of a laminate and rollers (4) for the longitudinal stretching of said laminate, characterized by at least one heated roller (5) mounted subsequently to said pair of grooved rollers (3).

21. An apparatus as claimed in Claim 20, characterized in that said heated roller (5) is placed in close proximity to the surface of one of the rollers of said pair of rollers (3).

22. An apparatus as claimed in Claim 20, characterized in that at least one conveyor roller is arranged between said pair or the last pair of grooved rollers (3) and said heated roller (5), and that the adjacent rollers in said assembly are in close proximity to one another that the laminate (2) is supported by a roller surface during substantially all of its travel from said pair or last pair of grooved rollers (3) to the heated roller (5).

23. An apparatus as claimed in Claim 20, characterized by a counter roller (6) located adjacent to the heated roller (5) for squeezing said laminate (2) in order to remove air bubbles entrapped between the laminate (2) and the surface of the heated roller (5).

24. An apparatus as claimed in Claim 23, characterized by a vibration drive for vibrating said counter roller (6) relatively to said heated roller (5).

### Patentansprüche

1. Verfahren zur Herstellung eines hochfesten Bahnmaterials, mit der Bildung eines Laminats, das mindestens zwei Schichten aus thermoplastischem Polymermaterial aufweist, wobei jede Schicht eine faserige Kornstruktur aufweist, die eine vorherrschende Richtung der Spaltbarkeit in jeder genannten Schicht liefert, die Schichten miteinander verklebt werden, und wobei die vorherrschenden Richtungen der Spaltbarkeit zueinander quer verlaufen, und mit der biaxialen Orientierung der Moleküle der Schichten durch Verstrecken der Schichten in im wesentlichen nicht axialen Schritten, wobei das querverlaufende Verstrecken dadurch bewirkt wird, daß man Druck auf die Oberfläche des Laminats längs Linien aufbringt, die sich im wesentlichen in Längsrichtung des Laminats erstrecken, um diesen eine wellige Ausbildung mitzuteilen, dadurch gekennzeichnet, daß man das biaxial orientierte Laminat einer Wärmebehandlung unterzieht, während man mindestens 7% Scrumpfung des Laminats mindestens in seiner Querrichtung stattfinden läßt, und daß man die Wärmebehandlung dadurch durchführt, daß man ein in Längsrichtung gefaltetes Laminat mit der Oberfläche eines heißen Körpers in Berührung bringt, wobei das Laminat der Oberfläche in in Längsrichtung gefaltetem Zustand zugeführt wird, wobei die Fältelung in einem solchen Ausmaß begrenzt wird, daß sie durch die Schrumpfung in der Querrichtung aufgehoben wird.

2. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß der beheizte Körper eine heiße Walze ist.

3. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß man auf den geheizten Körper ein Laminat aufbringt, das jene Ausbildung aufweist, die es während des letzten Querverstreckungsschrittes erhalten hat.

4. Verfahren nach Anspruch 3, dadurch gekennzeichnet, daß man das Laminat sich in Längsrichtung während des genannten, letzten Querverstreckungsschrittes zusammenziehen läßt.

5. Verfahren nach Anspruch 2, dadurch gekennzeichnet, daß Luftblasen, die zwischen dem Laminat und der Oberfläche der heißen Walze eingeschlossen sind, durch Quetschen entfernt werden, während man es dem Laminat ermöglicht, längs der Oberfläche der heißen Walze zu gleiten.

6. Verfahren nach Anspruch 5, dadurch gekennzeichnet, daß man das Laminat Schwingungen unterzieht, die kurze Intervalle aufweisen, während welcher das Laminat gegen die Oberfläche der heißen Walze angedrückt wird.

7. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß das thermoplastische Polymermaterial aus einer Mischung von 40 bis 85 Gew.-% an Polypropylen und 60 bis 15 Gew.-% an einer niedrighschmelzenden oder amorphen Beimischung besteht, welche

a) hauptsächlich aus Polyethylen inklusive dessen Kopolymeren besteht,

b) im wesentlichen dieselbe oder eine höhere Bruchdehnung aufweist als das Polypropylen, wenn es bei Raumtemperatur unter langsamer Dehnung geprüft wird,

c) einen Elastizitätsmodul aufweist, der bei Raumtemperatur gleich oder niedriger ist als jener einer Mischung aus 90% Polyethylen mit einer Dichte von 0,95 und 10% EPR, das 25% Ethylen und 75% Propylen enthält,

und wobei mindestens die letzten 25% der biaxialen Verstreckung, gemessen an der Flächenzunahme, bei

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weniger als 50°C vorgenommen werden, während der nachfolgende Schritt der Wärmebehandlung des biaxial orientierten Laminats bei einer Temperatur vorgesehen ist, die höher ist als 50°C und bevorzugt mindestens 70°C beträgt.

5 8. Verfahren nach Anspruch 7, dadurch gekennzeichnet, daß das Verstreckungsverhältnis in jeder Richtung und nach der Schrumpfung bestimmt nicht 2,5:1 überschreitet.

9. Verfahren nach Anspruch 7, dadurch gekennzeichnet, daß die Beimischung als ihre Hauptkomponente lineares Polyethylen aufweist.

10. Verfahren nach Anspruch 9, dadurch gekennzeichnet, daß das lineare Polyethylen ein hochdichtes Polyethylen mit einem Schmelzströmungsindex nach ASTM D 1238, Zustand E, ist, der 0,2 nicht  
10 überschreitet, und daß die Beimischung ferner zwischen 10 und 50% einer Weichmacherkomponente aufweist, bevorzugt eines Elastomers.

11. Verfahren nach Anspruch 7, dadurch gekennzeichnet, daß das lineare Polyethylen lineares Polyethylen mit niedriger Dichte ist.

12. Verfahren nach Anspruch 11, dadurch gekennzeichnet, daß der Schmelzströmungsindex des  
15 linearen Polyethylens mit niedriger Dichte nach ASTM D 1238, Zustand E, 3 nicht überschreitet.

13. Verfahren nach Anspruch 7, dadurch gekennzeichnet, daß man das Polyethylen so auswählt, daß seine Schrumpfungsfähigkeit bei 100°C in orientiertem Zustand höher ist als die entsprechende Schrumpfungsfähigkeit des Polypropylens.

14. Verfahren nach Anspruch 7, dadurch gekennzeichnet, daß man als Legierungsmittel zwischen dem  
20 Polypropylen und dem Polyethylen kleinere Mengen an verzweigtem Polypropylen beimischt, beispielsweise ein Kopolymer des Propylen und ein Polyolefin mit 4 oder mehr Kohlenstoffatomen.

15. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß die Richtung der Spaltbarkeit in jeder Schicht der Schichten des Laminats, das biaxial orientiert werden soll, einen Winkel von zwischen 10 und 35° zur Bearbeitungsrichtung des Laminats bildet.

25 16. Verfahren nach Anspruch 15, dadurch gekennzeichnet, daß das Verstreckungsverhältnis in jeder Richtung und nach der Schrumpfung bestimmt 2,5:1 nicht überschreitet.

17. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß das Laminat aus mindestens zwei getrennt extrudierten Folien aus thermoplastischem Polymermaterial gebildet ist, wobei jede Folie

30 a) eine Hauptlage hat, die eine faserige Kornstruktur aufweist, welche eine vorherrschende Richtung der Spaltbarkeit in jeder genannten Folie vorsieht, und

b) eine zweite Schicht zum Kontrollieren der Klebefestigkeit hat wobei die Folien miteinander so verklebt werden, daß die vorherrschenden Richtungen der Spaltbarkeit quer zueinander verlaufen, die zweite Schicht des einen Films der zweiten Schicht des anderen Films zugewandt ist und man die Moleküle der Schichten dadurch biaxial orientiert, daß man die Schichten in im wesentlichen einaxialen Schritten  
35 verstreckt, und wobei die Querverstreckung und die Verklebung dadurch bewirkt wird, daß man auf die Oberfläche des Laminats längs Linien einen Druck ausübt, die sich im wesentlichen in Längsrichtung des Laminats erstrecken, um diesem eine wellige Ausbildung mitzuteilen, und daß in diesen Hauptschichten die faserige Kornstruktur aus Mikrofibrillen aus hochkristallinem Polypropylen und/oder hochdichtem Polyethylen besteht, welche insgesamt in ein Matrixmaterial eingebettet sind, das vorwiegend aus  
40 Polypropylen mit niedriger Dichte besteht, und ferner dadurch gekennzeichnet,

a) daß das Matrixmaterial eine Bruchdehnung aufweist, die ähnlich oder höher als jene des die Fibrillen bildenden Polypropylens oder hochdichten Polyethylens ist, wenn dieses bei Raumtemperatur unter langsamer Dehnung geprüft wird, und

45 b) daß die zweiten Lagen hauptsächlich aus verzweigtem Polyethylen bestehen und eine Wärmeverklebungstemperatur aufweisen, die höher ist als 100°C, sowie eine Bruchdehnung, die ähnlich oder höher ist als jene des die Fibrillen bildenden Polypropylens oder hochdichten Polyethylens.

18. Verfahren nach Anspruch 17, dadurch gekennzeichnet, daß man das Laminat unter jener Temperatur wärmebehandelt, bei welcher die zweiten Lagen miteinander wärmeverkleben.

50 19. Verfahren nach Anspruch 18, dadurch gekennzeichnet, daß das Matrixmaterial einen Schmelzbereich aufweist, der niedriger ist als jener der zweiten Lage, und daß es dem Laminat während der genannten Wärmebehandlung gestattet ist, in mindestens der einen Richtung zu schrumpfen.

20. Vorrichtung nur zur Durchführung des Verfahrens nach Anspruch 1, mit mindestens einem Paar ineinander eingreifender, genuteter Walzen (3) zum Querverstrecken eines Laminats und Walzen (4) zum Längsverstrecken des Laminats, gekennzeichnet durch mindestens eine beheizte Walze (5), die dem Paar  
55 genuteter Walzen (3) nachfolgend angebracht ist.

21. Vorrichtung nach Anspruch 20, dadurch gekennzeichnet, daß die beheizte Walze (5) in enger Nachbarschaft zur Oberfläche einer der Walzen des Walzenpaares (3) angeordnet ist.

22. Vorrichtung nach Anspruch 20, dadurch gekennzeichnet, daß mindestens eine Förderwalze zwischen dem Paar oder dem letzten Paar genuteter Walzen (3) und der beheizten Walze (5) angeordnet ist,  
60 und daß die benachbarten Walzen in der genannten Anordnung in so enger Nähe zueinander angeordnet sind, daß das Laminat (2) während im wesentlichen seiner gesamten Bewegung von dem Paar oder dem letzten Paar der genuteten Walzen (3) zur beheizten Walze (5) von einer Walzenfläche getragen ist.

23. Vorrichtung nach Anspruch 20, gekennzeichnet durch eine Gegenwalze (6), die der beheizten Walze (5) benachbart angeordnet ist, um das Laminat (2) zu quetschen, um Luftblasen zu entschwärmen,  
65 die zwischen dem Laminat (2) und der Oberfläche der beheizten Walze (5) eingeschlossen sind.



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24. Vorrichtung nach Anspruch 23, gekennzeichnet, durch einen Schwingungsantrieb, um die Gegenwalze (6) relativ zur beheizten Walze (5) vibrieren zu lassen.

### Revendications

- 5 1. Procédé pour la fabrication d'un matériau en feuille de résistance élevée, comprenant la formation d'un stratifié comportant au moins deux couches d'un matériau polymère thermoplastique, chaque couche présentant une structure à grains fibrillaires déterminant une direction prédominante de capacité de fracturation dans chaque couche, les couches étant liées les unes aux autres alors que lesdites directions  
10 prédominantes de capacité de fracturation sont transversales les unes par rapport aux autres, et l'orientation biaxiale des molécules desdites couches en étirant les couches au cours d'étapes sensiblement uniaxiales, l'étirage transversal étant réalisé en appliquant une pression sur la surface du stratifié le long de lignes s'étendant sensiblement dans la direction longitudinale du stratifié pour lui conférer une configuration ondulée, caractérisé par le fait que le stratifié orienté biaxialement est soumis à  
15 un traitement thermique tout en permettant un retrait d'au moins 7% du stratifié dans au moins sa direction transversale, et que le traitement thermique est réalisé en amenant en contact un stratifié plissé longitudinalement avec la surface d'un corps chaud, le stratifié étant alimenté sur ladite surface à l'état plissé longitudinalement, le plissage étant limité de manière qu'il soit éliminé par ledit retrait dans la direction transversale.
- 20 2. Procédé selon la revendication 1, caractérisé en ce que ledit corps chauffé est un rouleau chaud.
3. Procédé selon la revendication 1, caractérisé par l'introduction sur le corps chauffé d'un stratifié ayant la configuration obtenue pendant la dernière étape d'étirage transversal.
4. Procédé selon la revendication 3, caractérisé en ce que le stratifié est autorisé à se contracter longitudinalement pendant ladite dernière étape d'étirage transversal.
- 25 5. Procédé selon la revendication 2, caractérisé en ce que des bulles d'air emprisonnées entre le stratifié et la surface du rouleau chaud sont éliminées par compression en autorisant le stratifié à glisser le long de la surface du rouleau chaud.
6. Procédé selon la revendication 5, caractérisé en ce que le stratifié est soumis à des vibrations avec de courts intervalles pendant lesquels le stratifié est appliqué à force contre la surface du rouleau chaud.
- 30 7. Procédé selon la revendication 1, caractérisé en ce que le matériau polymère thermoplastique consiste en un mélange de 40 à 85% en poids de polypropylène et de 60 à 15% en poids d'un mélange à faible point de fusion ou amorphe qui a) est constitué principalement de polyéthylène,  $\gamma$ , compris des copolymères de celui-ci, b) présente sensiblement le même allongement à la rupture ou un allongement supérieur à celui dudit polypropylène quand il est testé à la température ambiante et sous un faible étirage,  
35 c) présente un module d'élasticité qui, à la température ambiante, est égal à ou inférieur à celui d'un mélange de 90% de polyéthylène d'une densité de 0,95 et de 10% d'EPR contenant 25% d'éthylène et 75% de polypropylène, et dans lequel les derniers 25% au moins de l'étirage biaxial, mesurés sur l'acroissement de surface, sont réalisés au-dessous de 50°C, l'étape subséquente du traitement thermique du stratifié orienté biaxialement étant effectuée à une température supérieure à 50°C et de préférence d'au  
40 moins 70°C.
8. Procédé selon la revendication 7, caractérisé en ce que le rapport d'étirage dans une direction quelconque et déterminé après le retrait ne dépasse pas 2,5:1.
9. Procédé selon la revendication 7, caractérisé en ce que le mélange comprend en tant que composant principal un polyéthylène linéaire.
- 45 10. Procédé selon la revendication 9, caractérisé en ce que le polyéthylène linéaire est du polyéthylène haute densité dont l'indice d'écoulement à l'état fondu selon ASTM D 1238, condition E, ne dépasse pas 0,2 et en ce que le mélange comprend en outre entre 10 et 50% d'un composant d'amollissement, de préférence un élastomère.
11. Procédé selon la revendication 7, caractérisé en ce que le polyéthylène linéaire est un polyéthylène  
50 linéaire de basse densité.
12. Procédé selon la revendication 11, caractérisé en ce que l'indice d'écoulement à l'état fondu dudit polyéthylène linéaire basse densité selon ASTM D 1238, condition E, ne dépasse pas 3.
13. Procédé selon la revendication 7, caractérisé par la sélection du polyéthylène de manière que sa capacité de rétraction à 100°C, à l'état orienté, soit supérieure à la capacité de rétraction correspondante du  
55 polypropylène.
14. Procédé selon la revendication 7, caractérisé par le mélange, sous forme d'un agent d'alliage entre le polypropylène et le polyéthylène, de quantités mineures d'un polypropylène ramifié, par exemple un copolymère de propylène et de polyoléfine à 4 atomes de carbone ou plus.
15. Procédé selon la revendication 1, caractérisé en ce que la direction de la capacité de fracturation de  
60 chaque couche desdites couches du stratifié à orienter biaxialement forme un angle compris entre 10 et 35°C avec la direction du stratifié dans la machine.
16. Procédé selon la revendication 15, caractérisé en ce que le rapport d'étirage dans une direction quelconque et déterminé après retrait ne dépasse pas 2,5:1.
17. Procédé selon la revendication 1, caractérisé en ce que le stratifié est formé à partir d'au moins  
65 deux pellicules d'un matériau polymère thermoplastique extrudé séparément, chaque pellicule



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- comprenant a) une couche principale présentant une structure à grains fibrillaires déterminant une direction prédominante de capacité de fracturation dans chacune desdites pellicules, et b) une seconde couche pour contrôler la force d'adhérence, les pellicules étant reliées l'une à l'autre alors que lesdites directions prédominantes de capacité de fracturation sont transversales les unes par rapport aux autres, la
- 5 seconde couche d'une pellicule étant face à la seconde couche de l'autre pellicule, et par l'orientation biaxiale des molécules desdites couches par étirage des couches au cours d'étapes sensiblement uniaxiales, l'étirage transversale et la liaison étant réalisés en appliquant une pression sur la surface du stratifié le long de lignes d'étendant sensiblement dans la direction longitudinale du stratifié pour lui conférer une configuration ondulée, et dans lequel les couches principales à structure à grains fibrillaires
- 10 consistent en des micro-fibrilles d'un polypropylène cristallin élevé ou d'un polyéthylène haute densité, qui sont généralement noyées dans le matériau d'une matrice consistant de façon prédominante en un polyéthylène basse densité, et caractérisé en outre en ce que a) ledit matériau de la matrice présente un allongement à la rupture qui est similaire à ou supérieur à celui du polypropylène fibrillogène ou du polyéthylène haute densité quand il est testé à température ambiante sous un étirage lent, b) en ce que
- 15 lesdites secondes couches consistent principalement en un polyéthylène ramifié et présentent une température de jonction à chaud supérieure à 100°C et un allongement à la rupture semblable à ou supérieur à celui du polypropylène fibrillogène ou du polyéthylène haute densité.
18. Procédé selon la revendication 17, caractérisé par un traitement thermique du stratifié au-dessous de la température à laquelle les secondes couches se lient l'une à l'autre par la chaleur.
- 20 19. Procédé selon la revendication 18, caractérisé en ce que ledit matériau de la matrice présente une plage de fusion inférieure à celle de ladite seconde couche et le stratifié est autorisé à se rétracter, au moins dans une direction, pendant ledit traitement thermique.
20. Dispositif pour mettre en oeuvre seulement le procédé de la revendication 1, comprenant au moins une paire de rouleaux rainurés (3) engrenant l'un dans l'autre en vue de l'étirage transversal d'un stratifié,
- 25 et des rouleaux (4) pour l'étirage longitudinal dudit stratifié, caractérisé par le fait qu'au moins un rouleau chauffé (5) est monté à la suite de ladite paire de rouleaux rainurés (3).
21. Dispositif selon la revendication 20, caractérisé en ce que ledit rouleau chauffé (5) est placé à proximité étroite de la surface de l'un des rouleaux de ladite paire de rouleaux (3).
22. Dispositif selon la revendication 20, caractérisé en ce qu'au moins un rouleau convoyeur est
- 30 disposé entre ladite paire ou la dernière paire de rouleaux rainurés (3) et ledit rouleau chauffé (5), et en ce que les rouleaux adjacents dans ledit ensemble sont si proches les uns des autres que le stratifié (2) est supporté par une surface de rouleau pendant sensiblement tout son parcours depuis ladite paire ou la dernière paire de rouleaux rainurés (3) et le rouleau chauffé (5).
23. Dispositif selon la revendication 20, caractérisé par un contre-rouleau (6) situé proche du rouleau
- 35 chauffé (5) pour comprimer ledit stratifié (2) de façon à éliminer les bulles d'air emprisonnées entre le stratifié (2) et la surface du rouleau chauffé (5).
24. Dispositif selon la revendication 23, caractérisé par un mécanisme d'entraînement vibratoire pour faire fibrer ledit contre-rouleau (6) par rapport audit rouleau chauffé (5).

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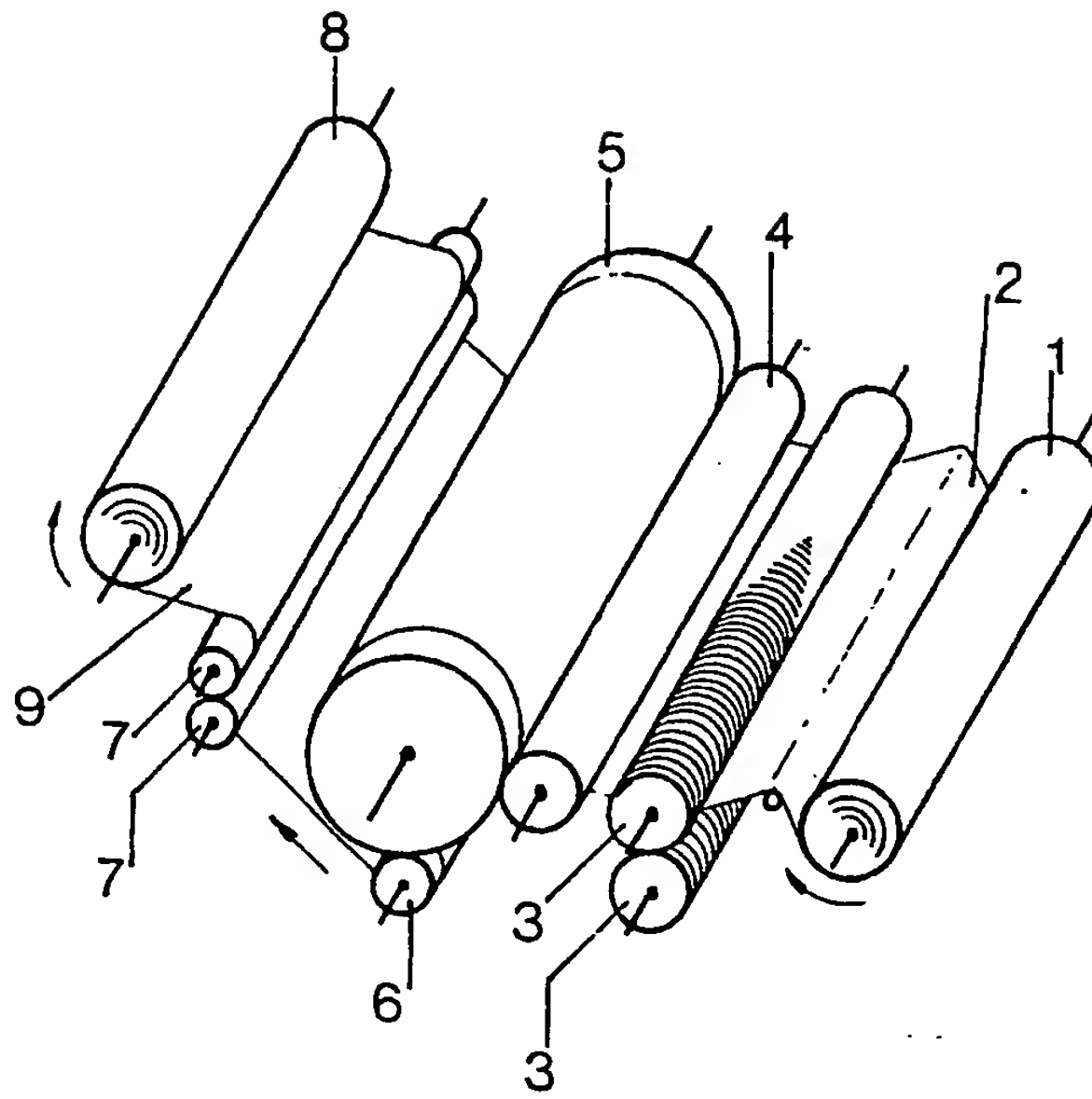


FIG.1

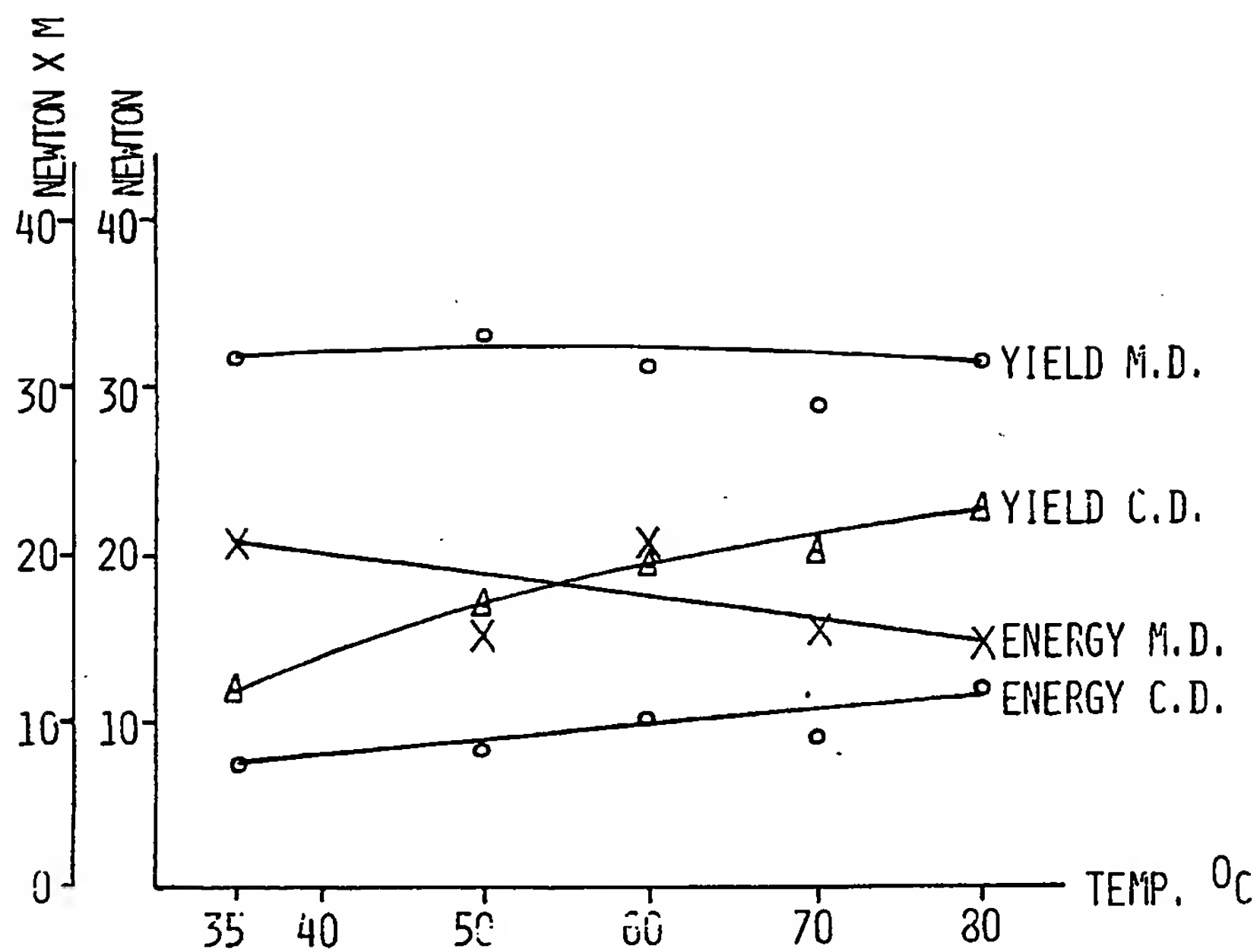


FIG. 2

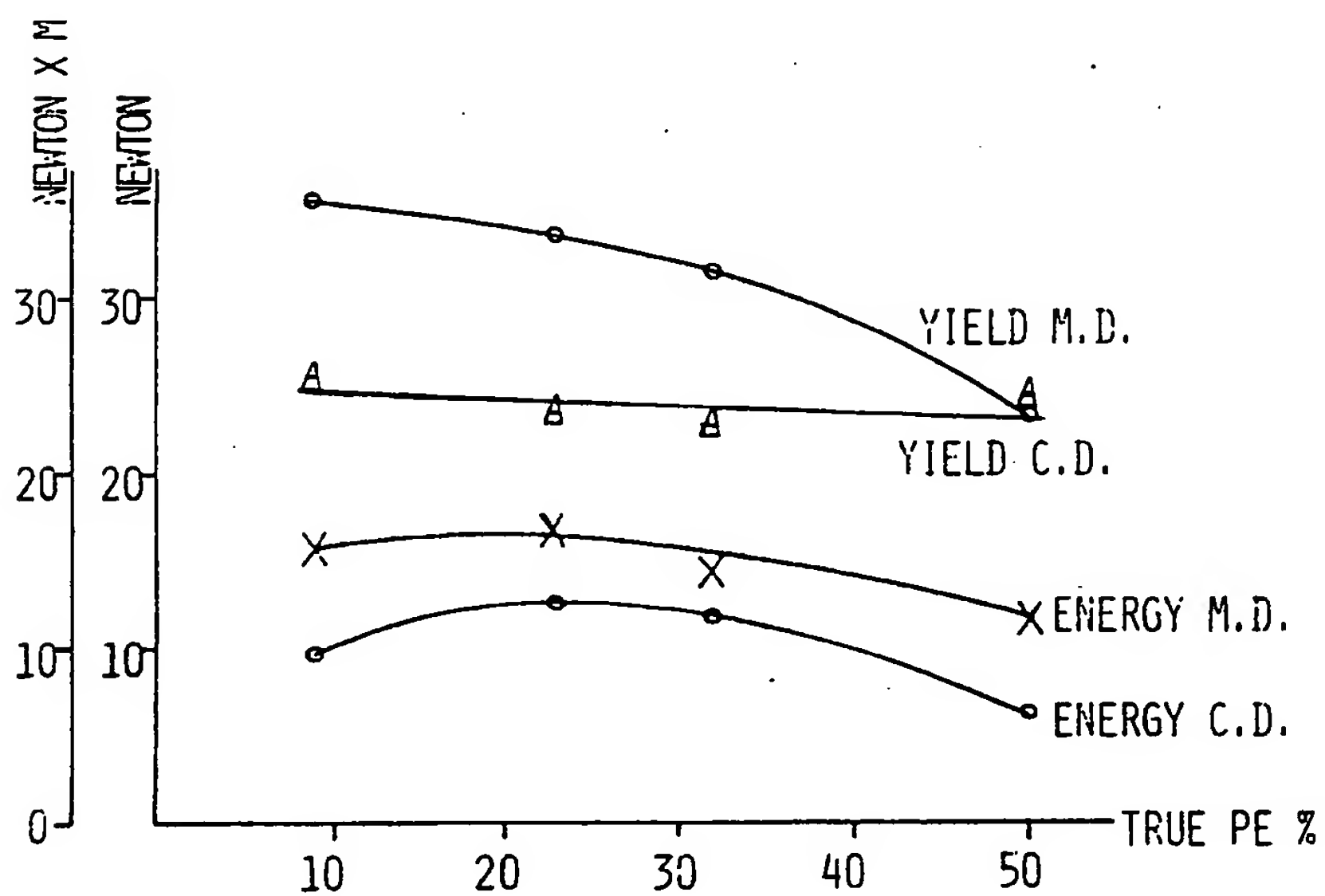


FIG. 3

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